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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the foaming masterbatch which uses a thermal-expansion nature microsphere as a principal component, and such a foaming masterbatch.

[0002]

[Description of the Prior Art] Since the elevated-temperature type thermal-expansion nature microsphere was developed in recent years, the foaming approach using a thermal-expansion nature microsphere came to be used widely. This foaming approach tends to obtain the moldings of a low consistency as a result by expanding the microsphere distributed in the shaping base material to hot forming and coincidence, and considering as a much more **** hollow solid sphere.

[0003] That is, this approach does not form a direct foaming opening into a base material. Therefore, a problem [as / in the approach of forming a foaming opening into a base material using a chemistry foaming agent or high pressure gas], i.e., problems, such as variation in cellular size or a free passage of air bubbles, is not produced. Moreover, the consistency and description of mold goods are controllable by this approach to arbitration by choosing the microsphere which has suitable expansion initiation temperature and dilatation, and choosing the particle size and the addition of a microsphere suitably. Therefore, there is an advantage that a desired foaming article is obtained with the sufficient yield. However, there are the following problems also in this approach.

[0004] That is, if distributed mixing of the microsphere is not fully carried out into the base material, since distribution of a hollow solid sphere (foaming microsphere) will become an ununiformity, properties, such as the mechanical strength of a foaming article and adiabatic, worsen. Moreover, if a microsphere is exposed to the temperature near expansion initiation temperature for a long time, since the phenomenon in which expand in advance and a particle comrade adheres each other will occur, homogeneity distribution becomes difficult. Furthermore, if exposed to the temperature beyond expansion peak temperature, husks will be torn and the function as a hollow solid sphere will be lost. For this reason, in order to obtain a good foaming article, while fully performing mixing with a microsphere and a base material and performing temperature management at the time of mixing proper, it is necessary to make a series of actuation until it results in hot forming complete promptly.

[0005] since it is alike, a microsphere is a minute spherical particle (before or after 15 micrometers) and a base material (thermoplastic polymer) is usually a 2-3mm comparatively large pellet type grain, the appropriate thing [mixing both to homogeneity in the state of an individual] is difficult. Moreover, generally the melting point of the resin used as the base material of a foaming article is high, and its melt viscosity is also large. Therefore, it is not easy to carry out homogeneity mixing of the microsphere at the base material of a melting condition, without being accompanied by prior expansion of a microsphere. Then, the approach of mixing a microsphere beforehand to the base material which is easy to mix for the purpose of aiming at improvement in the miscibility of a base material and a microsphere etc., and adding to a base material, just before fabricating a masterbatch, and nothing and this

masterbatch is adopted. Since it is easy to mix to a base material compared with carrying out mixed distribution of the direct microsphere according to this approach, it becomes possible after kneading of ultrashort time amount (about several minutes) to perform shaping.

[0006] However, as base material of this kind of masterbatch, ethylene vinyl acetate (EVA) is used conventionally. It is because EVA is comparatively fused at low temperature, so homogeneity mixing is possible, without being accompanied by prior expansion of a microsphere. However, since greasiness of EVA is strong, its miscibility at the time of masterbatch production is not enough. Moreover, the miscibility of a masterbatch and a base material is not enough, either. Furthermore, since EVA adheres to a mixer etc., a great effort is needed for cleaning of a machine. In addition, when a masterbatch is saved, blocking breaks out and there is a problem that handling nature worsens.

[0007] On the other hand, in the former, the suitable base material for which EVA can be substituted was not found out. For example, conventionally, since the melting point is high, polyethylene, polypropylene, etc. of a type cannot mix a microsphere easily in the state of melting. Moreover, conventionally, the polyethylene of a type etc. has a molecular weight distribution and large presentation distribution, and the smeariness component is included in the low-molecular-weight region. Therefore, this smeariness component becomes the cause of reducing the mechanical strength of a foaming article etc.

[0008]

[Problem(s) to be Solved by the Invention] It is made in view of the above, and with the low melting point, there are few smeariness components, and the miscibility and compatibility over a shaping base material choose good base material, and this invention aims at offering a foaming masterbatch with the sufficient user-friendliness which was excellent in foaming nature using this base material.

[0009]

[Means for Solving the Problem] The above-mentioned technical problem can make base material a special polyethylene system thermoplasticity polymer with a narrow molecular weight distribution and presentation distribution, and can attain a thermal-expansion nature microsphere by carrying out homogeneity mixing to this base material. Specifically, the following configurations can attain.

[0010] The thermal-expansion nature microsphere which consists of thermal-expansion nature matter confined in the interior of the husks with which invention according to claim 1 consists of thermoplastics, and these husks, The kneading process which kneads the base material which uses as a principal component the polyethylene system thermoplasticity polymer compounded using the single site catalyst, and is made with mixture, Extruding said mixture from an extruder, a hot cut is carried out and it is characterized by being the manufacture approach of a foaming masterbatch equipped with a pellet type and the foaming masterbatch pellet production process to make.

[0011] The polyethylene system thermoplasticity polymer compounded using the single site catalyst is what has the presentation distribution narrow molecular weight distribution and narrow in which the comonomer was distributed over homogeneity at each chain compared with what was conventionally compounded using the catalyst, i.e., multi-site catalyst, of a type. Therefore, even if it can produce the thing of the low melting point which is not in the former and is the thing of the low melting point, there are few low molecular weight constituents leading to smeariness.

[0012] Therefore, if such a polyethylene system thermoplasticity polymer is used as base material, troubles, such as a fall of adhesion on the trouble resulting from a smeariness component like a low melting point polymer conventional type [, such as EVA,], i.e., a stirring mixer machine, the blocking at the time of storage, a mixed defect with a shaping base material, and the mechanical strength of mold goods, are cancelable. Moreover, compared with a low melting point polymer conventional type [, such as EVA,], miscibility with a microsphere is good and excellent also in compatibility with the shaping base material which consists of olefin system resin etc. therefore, if such a foaming masterbatch is used, the engine performance of a foaming article will be markedly alike, and will improve.

[0013] Furthermore, in this invention, the foaming masterbatch which used such a polyethylene system thermoplasticity polymer is processed into a pellet type by the hot cut method. Since the resin which generally serves as a shaping base material is also processed into a pellet type while being able to use

simple that it is the foaming masterbatch of a pellet type, dryblend nature with a shaping base material is good.

[0014] Invention according to claim 2 is characterized by being beyond the DSC peak temperature of said polyethylene system thermoplasticity polymer, and heating the mixture in said mixed process in the temperature below the expansion initiation temperature of said microsphere in the manufacture approach of a foaming masterbatch according to claim 1.

[0015] A melting polymer and a microsphere can be mixed to homogeneity, without being accompanied by prior expansion of a microsphere, if it is this configuration.

[0016] Invention according to claim 3 is characterized by said base material containing the liquid paraffin of the amount which can make said microsphere become wet in the manufacture approach of a foaming masterbatch according to claim 1 or 2.

[0017] When making a polyethylene system thermoplasticity polymer carry out mixed distribution of the microsphere, the phenomenon where the microsphere which is a minute particle soars into air in the early stages of mixing arises. In here, if a liquid paraffin is made to exist in extent with which a microsphere becomes wet, the microsphere at the time of stirring mixing will dance, and a riser can be prevented, and it will act so that a liquid paraffin may raise the compatibility of a microsphere and a polyethylene system thermoplasticity polymer. Therefore, stirring mixing actuation with a polyethylene system thermoplasticity polymer and a microsphere becomes easy.

[0018] Invention according to claim 4 is characterized by including the water for cooling in the mixture in said mixed process in the manufacture approach of claim 1 thru/or a foaming masterbatch given in three.

[0019] When the melting temperature of base material is close to the expansion initiation temperature of a microsphere (or more than it), in order to prevent prior expansion of a microsphere on the occasion of mixing with base material and a microsphere, it is necessary to complete mixing by ultrashort time amount (around 1 - 5 minutes), and to lower the temperature of mixture promptly. Here, if little water is included in mixture, this water will be evaporated with the heat of mixture and heat of vaporization will be taken in that case. Therefore, the temperature of mixture can be reduced promptly. It is good to consider as the amount which carries out evaporation evaporation and does not remain in mixture as an amount of the water added into mixture, and it is desirable to determine the amount in relation with the temperature of mixture. That is, since the amount of evaporation evaporation is large when the temperature of mixture is high, it considers as more amounts, and when the temperature of mixture is low, suppose that it is little.

[0020] In the manufacture approach of claim 1 thru/or a foaming masterbatch given in four, invention according to claim 5 will be characterized by being what has the property in which husks explode within 5 minutes, if said microsphere starts expansion at the temperature of 90 degrees C or more in ordinary pressure and is heated by the temperature of 220 degrees C or more.

[0021] If the expansion initiation temperature of a microsphere is too low, while expanding easily with the stirring heat at the time of mixing with base material, if too high, the original purpose of use made to foam to hot forming and coincidence cannot fully attain. Considering this, the expansion initiation temperature of a microsphere has good 90 degrees C or more. If it is the microsphere which does not explode on the other hand even if heated by the elevated temperature, temperature conditions will not take special cautions.

[0022] However, such [actually] a microsphere does not exist. This invention aims at raising the user-friendliness nature of the usual microsphere which exists actually. If such a microsphere starts expansion at the temperature of 90 degrees C or more in ordinary pressure and is heated by the temperature of 220 degrees C or more, husks will explode within 5 minutes. That is, if the requirements for a configuration of said base material concerning this invention start expansion at the temperature of 90 degrees C or more and are heated by the temperature of 220 degrees C or more, they have a special meaning in the microsphere with which husks explode within 5 minutes.

[0023] Invention according to claim 6 is characterized by being what the husks of said microsphere become from the copolymer containing acrylonitrile in the manufacture approach of claim 1 thru/or a

foaming masterbatch given in five.

[0024] Where the thermal-expansion nature matter is confined in the interior of husks in a microencapsulation means as it is a copolymer containing acrylonitrile, -izing can be carried out [****], and in ordinary pressure, expansion is started at the temperature of 90 degrees C or more, and it can do with a stable coat to the temperature near 220 degree C.

[0025] Invention according to claim 7 is characterized by the thermal-expansion nature matter of said microsphere being an isopentane or an isobutane in the manufacture approach of claim 1 thru/or a foaming masterbatch given in six.

[0026] Since the expansion pressure force is large in the temperature around 90 degrees C - 220 degrees C in it being the microsphere with which the isopentane or the isobutane was used as thermal-expansion nature matter, a suitable foaming masterbatch is obtained.

[0027] Invention according to claim 8 is characterized by said single site catalyst being a compound catalyst containing the metallocene compound and methyl aluminoxane of 4 group transition metals in the manufacture approach of claim 1 thru/or a foaming masterbatch given in seven.

[0028] The thing of the low melting point is obtained as it is the polyethylene system thermoplasticity polymer compounded using the compound catalyst of this configuration, and molecular weight distribution and presentation distribution of a comonomer will become narrow. Therefore, it is suitable as base material of a foaming masterbatch.

[0029] Invention according to claim 9 is characterized by said polyethylene system thermoplasticity polymer being polyethylene in the manufacture approach of a foaming masterbatch according to claim 1 to 8.

[0030] The polyethylene compounded with the single site catalyst has low crystallinity, and becomes what has a narrow molecular weight distribution, and what has a few smeariness component is obtained with the low melting point. Such polyethylene especially is suitable as base material of a foaming masterbatch.

[0031] The foaming masterbatch manufactured by the manufacture approach of the foaming masterbatch the one to claim 9 above-mentioned publication can be specified also as invention of an object.

[0032] That is, invention according to claim 10 is a foaming masterbatch which consists of a thermal-expansion nature microsphere which consisted of thermal-expansion nature matter confined in the interior of the husks which consist of thermoplastics, and these husks, and base material which uses as a principal member the polyethylene system thermoplasticity polymer compounded using the single site catalyst.

[0033] Invention according to claim 11 has the property in which the husks with which said microsphere starts expansion at the temperature of 90 degrees C or more in ordinary pressure, and shuts up the thermal-expansion nature matter within 5 minutes in the temperature of 220 degrees C or more explode, in a foaming masterbatch according to claim 10.

[0034] In a foaming masterbatch according to claim 10 or 11, as for invention according to claim 12, said polyethylene system thermoplasticity polymer has DSC peak melting temperature in a low temperature side rather than the expansion initiation temperature of said microsphere.

[0035] Invention according to claim 13 consists of a copolymer in which the husks of said microsphere contain acrylonitrile in claim 10 thru/or a foaming masterbatch given in 12.

[0036] In claim 10 thru/or a foaming masterbatch given in 13, the thermal-expansion nature matter of said microsphere of invention according to claim 14 is an isopentane or an isobutane.

[0037] Invention according to claim 15 is a compound catalyst in which said single site catalyst contains the metallocene compound of 4 group transition metals, and methyl aluminoxane in claim 10 thru/or a foaming masterbatch given in 14.

[0038] In claim 10 thru/or a foaming masterbatch given in 15, said polyethylene system thermoplasticity polymer of invention according to claim 16 is polyethylene.

[0039] In claim 10 thru/or a foaming masterbatch given in 16, as for invention according to claim 17, it comes to process said foaming masterbatch into a pellet type with a diameter [of 1mm - 5mm], and a die length of 1mm - 5mm.

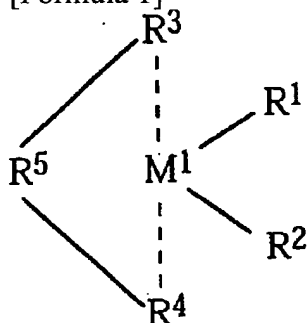
[0040]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained.

[0041] First, the single site catalyst as used in this specification means what has the uniform property of the active spot which lives together. As a single site catalyst, ** 1 (metallocene complex) is mentioned, for example. Moreover, the compound catalyst (when calling it a metallocene catalyst below, this compound catalyst is included) which combined the compound (aluminoxane) shown in the metallocene complex of ** 1 at ** 2 is mentioned. Such a metallocene catalyst is well-known, for example, it is indicated by official reports, such as JP,5-140227,A, JP,5-140228,A, JP,5-209019,A, and JP,5-209019,A, and having the descriptions, like the polyethylene system thermoplasticity polymer compounded using these metallocene catalysts has molecular weight distribution and narrow presentation distribution is known.

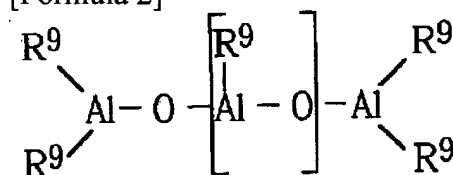
[0042]

[Formula 1]



[0043]

[Formula 2]



[0044] It sets to ** 1 and is M1. Titanium, a zirconium, a hafnium, BANAJIUMU, niobium or a tantalum -- it is -- R1 And R2 You may differ, even if mutually the same. The alkyl group of a hydrogen atom, a halogen atom, and the carbon atomic numbers 1-10, the alkoxy group of the carbon atomic numbers 1-10, The aryl group of the carbon atomic numbers 6-10, the aryloxy group of the carbon atomic numbers 6-10, The alkenyl radical of the carbon atomic numbers 2-10, the arylated alkyl radical of the carbon atomic numbers 7-40, They are the alkyl aryl radical of the carbon atomic numbers 7-40, or the aryl alkenyl radical of the carbon atomic numbers 8-40. R3 And R4 Same [mutually], it differs and is the central metal atom M1. It is the single nucleus or polynuclear hydrocarbon residue which can form the complex of sandwich structure.

[0045] R5 =BR6, =AlR6, -germanium-, -Sn-, -O-, -S-, =SO, =SO2, =NR6, =CO, and =PR6 Or it is P(O) R6 (however, R6 a hydrogen atom, a halogen atom). R9 [moreover,] You may differ, even if mutually the same, and it is the alkyl group of the carbon atomic numbers 1-6, the fluoro alkyl group of the carbon atomic numbers 1-6, the aryl group of the carbon atomic numbers 6-18, the fluoro aryl group of the carbon atomic numbers 6-18, or a hydrogen atom, and n is the integer of 0-50.

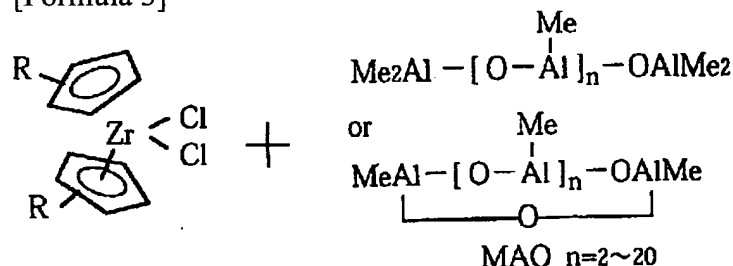
[0046] The example of the compound catalyst which consists of a compound of ** 1 and ** 2 is shown in ** 3. The polyethylene system thermoplasticity polymer compounded using the compound catalyst which combined the compound (2 chlorination zirconocene) which made the ligand the cyclopentadiene shown in the left of ** 3, and the aluminoxane compound shown in the right of ** 3 is suitable as base material concerning this invention. Molecular weight distribution are narrow, and a comonomer becomes what (presentation distribution is narrow) was distributed over homogeneity at each chain, and

since there are few contents of a low molecular weight constituent or a smeariness component, the polyethylene system thermoplasticity polymer compounded using this compound catalyst makes this polymer base material, and is made with what the fall of the mechanical strength of the foaming article which originates that it is the foaming masterbatch which comes to mix a microsphere to this base material in a low molecular weight constituent or a smeariness component does not produce.

[0047] In addition, multi-site catalysts, such as a Ziegler type catalyst widely used as a polymerization reaction catalyst from the former, have the active spot of various structures. Therefore, the polymer compounded using such a catalyst becomes what has large molecular weight distribution and presentation distribution. Therefore, in such a polymer, it cannot make with a suitable masterbatch.

[0048]

[Formula 3]



[0049] the polyethylene system thermoplasticity polymer compounded as base material concerning this invention using the above-mentioned single site catalyst -- using it -- concrete -- for example, Dow Chemical Japan Co., Ltd. -- The shrine trade names AFFINITY and ENGAGE (ethylene octene copolymer) are used.

[0050] As described above, the thing of the low melting point fused below at the expansion initiation temperature of a microsphere as it is the polyethylene system thermoplasticity polymer compounded using the single site catalyst is obtained. Moreover, since a molecular weight distribution and presentation distribution are narrow even if it is the thing of the low melting point, there are few smeariness components. Furthermore, while the viscosity at the time of melting is small, it is because the reinforcement at the time of hardening is strong.

[0051] It is desirable to use what has the melting point which are the above polyethylene system thermoplasticity polymers, and is defined as a low temperature side at DSC (differential scanning calorimetry) peak temperature rather than the expansion initiation temperature of a thermal-expansion nature microsphere by this invention. It is because a microsphere expands by the heat of fusion when the melting point of base material was higher than the expansion initiation temperature of a microsphere and it mixes a microsphere in the state of melting, so it cannot do with a good foaming masterbatch.

[0052] On the other hand, as a microsphere which is another principal member of a foaming masterbatch, although various kinds of microspheres are usable, husks are formed by the copolymer containing acrylonitrile and, generally use the microcapsule (microsphere) which confined the isopentane or the isobutane in the interior. It is because the copolymer containing acrylonitrile is excellent in the field of thermoplasticity, and reinforcement and ductility, and an isopentane and an isobutane are excellent in the field of an expansion coefficient and the expansion pressure force and suitable as a principal member of this kind of foaming masterbatch.

[0053] It is good to extrude and carry out the hot cut of said mixture to the kneading process which the manufacture approach of this invention makes the above polyethylene system thermoplasticity polymers base material, and kneads the microsphere of thermal-expansion nature to this from a dice, to make the minimum of the temperature at the time of kneading in this manufacture approach (temperature of mixture) into the DSC peak temperature of base material, although it has a pellet and the foaming masterbatch pellet production process to make, and to make an upper limit into the expansion initiation temperature of a microsphere. Thus, if the temperature at the time of manufacture is set up, since a microsphere is mixable to the base material of a melting condition, uniform mixing can make.

Moreover, since the temperature at the time of this kneading is below the expansion initiation temperature of a microsphere, a microsphere does not expand in advance.

[0054] By the way, as for a thermal-expansion nature microsphere, what has the property in which the husks which started expansion and shut up the thermal-expansion nature matter within 5 minutes in the temperature of at least 220 degrees C or more in ordinary pressure at the temperature of 90 degrees C or more explode is common. Since there is a possibility of expanding with the heat (heat of mixing) generated at the time of mixing as expansion initiation temperature is less than 90 degrees C, it is because 90 degrees C or more are suitable as expansion initiation temperature, and when taking into consideration the usual heating molding temperature of another side and a foaming article, what has expansion peak temperature near 220 degree C is desirable. It is because handling nature will worsen on the contrary if expansion peak temperature is set as the place exceeding 220 degrees C. In addition, if a microsphere stops at the temperature beyond expansion peak temperature for a long time, it will explode with internal pressure and will lose the function.

[0055] On the other hand, if the property of a microsphere is above, as the melting point (DSC peak temperature) of the polyethylene system thermoplasticity polymer which is base material, it is 220 degrees C or less, and 90 degrees C or less are preferably good. the case where a microsphere is mixed with the melting temperature of base material as it is the base material which is not fused at the expansion peak temperature or expansion initiation temperature of a microsphere -- a microsphere -- a burst -- or it is because it expands in advance.

[0056] If the melting point of the polyethylene as one of these and base material is too low, a masterbatch will soften in a summer etc. and handling nature will worsen. Moreover, it becomes easy to produce adhesion in a mixer, and a masterbatch comrade's blocking. Therefore, as melting point temperature of base material, 220 degrees C or less 120 degrees C or less are more preferably made into 90 degrees C or less above 50 degrees C above 50 degrees C above 50 degrees C.

[0057] In addition, although acquisition of the microsphere which does not expand in advance at the temperature exceeding 120 degrees C is not easy, the microsphere which has expansion initiation temperature near 120 degree C is marketed. Therefore, a foaming masterbatch can be produced, without being accompanied by prior expansion, if the melting point of base material is 120 degrees C or less. However, to use base material with a melting point of 120 degrees C, it is necessary to knead extremely for a short time.

[0058] furthermore, the thermoplastic elastomer olefin with which, as for the polyethylene system thermoplasticity polymer compounded using said single site catalyst carried out although base material is excellent in compatibility with the base material which constitutes a foaming article, they mixed plastomers, such as polyethylene, polypropylene, and ethylene vinyl acetate, and polypropylene and EPR, for example since there were few low molecular weight constituents -- compatibility with shaping base materials, such as a SEBS type and SEPS type styrene thermoplastic elastomer, is still better. Therefore, the foaming article produced using the foaming masterbatch which starts this invention to these base materials is excellent also in a mechanical strength as well as lightweight nature, adiathermic, etc.

[0059] Next, the production approach of the foaming masterbatch concerning this invention is explained.

[0060] First, said polyethylene system thermoplasticity polymer as a principal member of base material is heated more than the melting point (usually 50 degrees C - 90 degrees C), and is fused. To this melting polyethylene system thermoplasticity polymer, a thermal-expansion nature microsphere is added ten to 70% of the weight, and it mixes about 1 minute by the mixer. As stirring reinforcement of a mixer, a microsphere considers as extent which is not destroyed by shearing force, and shortens mixing time as much as possible. It is because damage on the husks of a microsphere will become large and fear of prior expansion will increase by the stirring heat of mixing, if mixing time becomes long.

[0061] Subsequently, mixture is extruded from a dice, a hot cut is carried out to suitable die length, and it makes with a pellet. Thereby, the foaming masterbatch pellet concerning this invention is producible. Here, it is desirable to make it the same size as a shaping base material pellet as pellet size. It is because

it will be easy to carry out homogeneity mixing with dryblend if a base material and size are the same. What is necessary is just to consider as the diameter of 1mm - 5mm, and die length of 1mm - 5mm as size of a foaming masterbatch pellet generally. In addition, since it is easy to block the pellet just behind a hot cut, forced cooling is carried out if needed.

[0062] In the above-mentioned manufacture approach, it is good to add the liquid paraffin of optimum dose preferably at the time of mixing with base material and a microsphere. Although the microsphere which is a minute particle produces the phenomenon which soars into air on the occasion of stirring, it is because this liquid paraffin will change a microsphere into the condition of having become wet if the liquid paraffin of optimum dose exists, so it dances and a riser can be prevented. Moreover, it is because a liquid paraffin raises the compatibility of a microsphere and a polyethylene system thermoplasticity polymer, so mixed effectiveness increases and homogeneity mixing is realized by short-time stirring mixing.

[0063] Furthermore, in the above-mentioned manufacture approach, it is good to add into mixture by using little water as a cooling agent. Because, if little water is added into the mixture of base material and a microsphere (and liquid paraffin), since this water will evaporate and evaporate and heat will be taken from mixture, it can prevent that mixture becomes an abnormality elevated temperature with the shear heat at the time of mixing. Thereby, prior expansion of a microsphere can be controlled. In addition, it considers as the amount which evaporates and evaporates as an amount of the water added into mixture. If it is water of optimum dose, since it will not remain, it does not have a bad influence on mold goods.

[0064] By the way, it makes with a foaming article, or as a use gestalt of the foaming masterbatch of this invention, add to the shaping base material which carried out melting just before shaping, extrude in metal mold at 170 to 200 degree C after short-time kneading, it is made to foam to coincidence, injection molding is carried out at 150 to 180 degree C, and a foaming article is produced. as the shaping base material used here -- low density polyethylene and a line -- low density polyethylene, high density polyethylene, polypropylene, ethylene butadiene acrylonitrile, ethylene and vinyl acetate, polystyrene, a plasticization vinyl chloride, a styrene block copolymer, styrene, etc. are mentioned.

[0065] In addition, the microsphere in a masterbatch ends expansion in about 2 minutes from 30 seconds, when heated beyond expansion initiation temperature. Therefore, when kneading and cycle time with a base material become long, it is necessary to set up temperature low. On the other hand, when kneading and molding temperature are high, a foaming masterbatch is added just before hot forming, and shaping is completed as promptly as possible. However, since excessive frictional heat occurs and a microsphere may be destroyed on the contrary when it speeds up [extrusion] too much, it is careful.

[0066] The main components of this invention are explained further. the line which compounded drawing 1 and drawing 2 using the single site catalyst (metallocene catalyst) -- low density polyethylene (LLDPE) and the line using a multi-site catalyst (conventional catalyst) -- the molecular weight distribution in low density polyethylene, and a consistency and DSC peak melting temperature are shown typically.

[0067] The polymer using a single site catalyst has narrow molecular weight distribution as compared with the case where a catalyst is used conventionally so that clearly from drawing 1 . Moreover, to there being an inclination for the melting point to hardly fall even if a consistency falls, by the polymer using a single site catalyst, DSC peak melting temperature falls according to the fall of a consistency, and it has the overall more low melting point by the case where a catalyst is used conventionally so that clearly from drawing 2 . These things show that the polymer compounded using the single site catalyst is suitable as base material of the foaming masterbatch concerning this invention.

[0068] Drawing 3 is one instantiation of the temperature-expansion curve of the thermal-expansion nature microsphere used by this invention. As shown in drawing 3 , the temperature-expansion curve of a thermal-expansion nature microsphere is drawing the parabola. That is, since the husks of a microsphere will be destroyed if heated beyond predetermined temperature, the volume reduces a thermal-expansion nature microsphere on the contrary. Considering this, the melting point of the base

material which composes a foaming masterbatch is understood are good to be chosen proper in the relation between the expansion initiation temperature of a microsphere, and expansion peak temperature (burst temperature), and to determine a suitable foaming masterbatch presentation in consideration of the temperature at the time of hot forming of a shaping base material.

[0069]

[Example] Based on an example, this invention is explained concretely below.

[0070] [Example 1] As a thermal-expansion nature microsphere, Expancel 092DU-120 made from Expancel (the grain size of three - 50 micrometers, the relative density of 1.2g/cc, 118 to 126 degree C expansion initiation temperature, 188 to 195 degree C destructive temperature) was prepared. Moreover, as a polyethylene system polymer compounded using the single site catalyst, he is Dow Chemical Japan, Inc. Shrine ENGAGE SM8400 (the consistency of 0.870g/cc, comonomer seriousness of 24%, DSC peak melting point of 63.3 degrees C) was prepared.

[0071] Above ENGAGE Mixing for about 1 minute was performed by the agitating speed (about 360 rpm) which supplies 70kg and a liquid paraffin into 0.2kg, supplies Expancel 092DU-120 to the super mixer (Product made from KATAWA) of capacity 500L in 30kg order, and does not carry out the temperature rise of SM8400 to 60 degrees C or more.

[0072] Subsequently, what was mixed above was put into the biaxial screw extruder (IKEGAI company make; GT-110), and it kneaded on conditions with a temperature [of screw-speed 30rpm and the dice section] of 90 degrees C, and extruded in diameter of 3-3.5mm. And the hot cut of what was extruded from the dice was immediately carried out with the rotation hammer attached in the dice outlet. Furthermore, the pellet just behind a hot cut was cooled until it became the temperature of 50 degrees C or less, putting into the pellet cooler equipped with the body of revolution of six square shapes, and rotating it. It is because it adheres mutually if the temperature of the pellet just behind a hot cut is close to melting temperature and it remains as it is.

[0073] The foaming masterbatch pellet which starts this invention with a diameter [of 3-3.5mm] and a die length of 2mm - 4mm as mentioned above was produced. In addition, the size of a foaming masterbatch pellet is good to double with the pellet size of the partner resin (base material) which performs foaming. It is because dryblend becomes it easy that pellet size is the same.

[0074] After carrying out the dryblend of the 10kg (Tokuyama MS670) of the polypropylene resin of the conventional type compounded in foaming masterbatch pellet 1kg produced above using the multi-site catalyst, injection molding (the nozzle temperature of about 165 degrees C, die temperature of 40-80 degrees C) was carried out, the foaming article was produced, and the description was observed. Consequently, the appearance condition is good and homogeneity and a good foaming condition were observed by magnifier observation of the fracture surface.

[0075] [Example 2] as a microsphere of thermal-expansion nature As a polyethylene system polymer compounded using another side and a single site catalyst, using said Expancel 092DU-120 Said ENGAGE SM1250 (the consistency of 0.885g/cc) It replaces with SM8400 and he is Dow Chemical Japan. Shrine AFFINITY The foaming masterbatch of the presentation shown in Table 1 which added paraffin oil and water further was produced using the comonomer seriousness of 19%, and the DSC peak melting point of 85.3 degrees C.

[0076]

[Table 1]

Presentation Loadings (% of the weight)

----- AFFINITY SM1250 70 Expancel 092DU-120 30 Paraffin oil 2 Liquid paraffin

0.5 Water 2 [0077] At the foaming masterbatch of this example 2, it is said ENGAGE. AFFINITY with the melting point higher than SM8400 (DSC peak melting point of 63.8 degrees C) SM1250 (DSC peak melting point of 85.3 degrees C) was used. For this reason, the temperature of the dice section was kneaded as 100 degrees C (an example 1 90 degrees C). And in order to prevent that a microsphere expands in advance with the temperature at the time of kneading, and the engine performance deteriorates, 2% of the weight of water was added into mixture. This water evaporates, when mixture is extruded from a dice, and it takes heat of vaporization. Therefore, since the temperature of a foaming

masterbatch pellet falls quickly, the heat deterioration (prior expansion) of Expancel 092DU-120 can be prevented. In addition, since this water is evaporated, it does not remain in ** let.

[0078] Thus, using the foaming masterbatch pellet concerning the produced example 2, the foaming article was produced like the example 1 and the description was investigated. Consequently, it was checked that a good foaming article is obtained.

[0079]

[Effect of the Invention] In this invention, the polyethylene system thermoplasticity polymer of the low melting point compounded using the single site catalyst is used as base material of a foaming masterbatch. Since a molecular weight distribution and presentation distribution are narrow in it being such a polyethylene system thermoplasticity polymer, even if it is the thing of the low melting point, there are few smeariness components. Therefore, since it is easy to mix a minute microsphere and there is nothing in solid **, there is no adhesion to a mixer etc. Furthermore, since blocking between pellets is not produced even if it pelletizes, it can do with a shaping base material and a foaming masterbatch pellet with the sufficient user-friendliness which can carry out dryblend.

[0080] In addition to the above-mentioned advantage, the polyethylene system thermoplasticity polymer compounded using the single site catalyst is excellent also in compatibility with a foaming base material. therefore, quality, such as a mechanical strength of a foaming article, is markedly alike, and improves.

[0081] As mentioned above, according to this invention, a foaming masterbatch pellet with the sufficient user-friendliness excellent in foaming nature (cubical-expansion nature) is obtained, and the remarkable effectiveness that it can contribute to expansion of the use application of the fizz mold goods which use a thermal-expansion nature microsphere and such a microsphere as a component is acquired according to . which can aim at improvement of the productivity of a foaming article, improvement in quality, etc. by using this foaming masterbatch pellet, therefore this invention.

[Translation done.]

* NOTICES *

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the foaming masterbatch which carries out a hot cut to mixture and the kneading process to make, extruding said mixture from an extruder, and is equipped with a pellet type and the foaming masterbatch pellet production process to make by kneading the thermal-expansion nature microsphere which consists of thermal-expansion nature matter confined in the interior of the husks which consist of thermoplastics, and these husks, and the base material which uses as a principal component the polyethylene system thermoplasticity polymer compounded using the single site catalyst.

[Claim 2] The manufacture approach of the foaming masterbatch according to claim 1 characterized by being beyond the DSC peak temperature of said polyethylene system thermoplasticity polymer, and heating the mixture in said mixed process to the temperature below the expansion initiation temperature of said microsphere.

[Claim 3] The manufacture approach of the foaming masterbatch according to claim 1 or 2 characterized by said base material containing the liquid paraffin of the amount which can make said microsphere become wet.

[Claim 4] The manufacture approach of the foaming masterbatch of claim 1 thru/or 3 publications characterized by including the water for cooling in the mixture in said mixed process.

[Claim 5] The manufacture approach of the foaming masterbatch of claim 1 thru/or 4 publications which are what has the property in which husks will explode within 5 minutes if said microsphere starts expansion at the temperature of 90 degrees C or more in ordinary pressure and is heated by the temperature of 220 degrees C or more.

[Claim 6] The manufacture approach of the foaming masterbatch according to claim 1 to 5 which is what the husks of said microsphere become from the copolymer containing acrylonitrile.

[Claim 7] The manufacture approach of a foaming masterbatch according to claim 1 to 6 that the thermal-expansion nature matter of said microsphere is an isopentane or an isobutane.

[Claim 8] The manufacture approach of a foaming masterbatch according to claim 1 to 7 that said single site catalyst is a compound catalyst containing the metallocene compound and methyl aluminoxane of 4 group transition metals.

[Claim 9] The manufacture approach of a foaming masterbatch according to claim 1 to 8 that said polyethylene system thermoplasticity polymer is polyethylene.

[Claim 10] The foaming masterbatch which consists of a thermal-expansion nature microsphere which consisted of thermal-expansion nature matter confined in the interior of the husks which consist of thermoplastics, and these husks, and base material which uses as a principal member the polyethylene system thermoplasticity polymer compounded using the single site catalyst.

[Claim 11] Said microsphere is a foaming masterbatch according to claim 10 which is what has the property in which the husks which start expansion at the temperature of 90 degrees C or more in ordinary pressure, and shut up the thermal-expansion nature matter within 5 minutes in the temperature of 220 degrees C or more explode.

[Claim 12] The foaming masterbatch according to claim 10 or 11 said whose polyethylene system thermoplasticity polymer is what has DSC peak melting temperature in a low temperature side rather than the expansion initiation temperature of said microsphere.

[Claim 13] Claim 10 which the husks of said microsphere become from the copolymer containing acrylonitrile thru/or a foaming masterbatch given in 12.

[Claim 14] The foaming masterbatch of claim 10 thru/or 13 publications whose thermal-expansion nature matter of said microsphere is an isopentane or an isobutane.

[Claim 15] The foaming masterbatch of claim 10 thru/or 14 publications said whose single site catalysts are compound catalysts containing the metallocene compound of 4 group transition metals, and methyl aluminoxane.

[Claim 16] The foaming masterbatch of claim 10 thru/or 15 publications said whose polyethylene system thermoplasticity polymers are polyethylene.

[Claim 17] The foaming masterbatch of claim 10 thru/or 16 publications said whose foaming masterbatches are the things which it comes to process into a pellet type with a diameter [of 1mm - 5mm], and a die length of 1mm - 5mm.

[Translation done.]

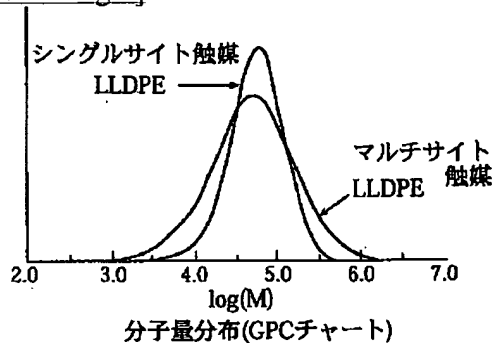
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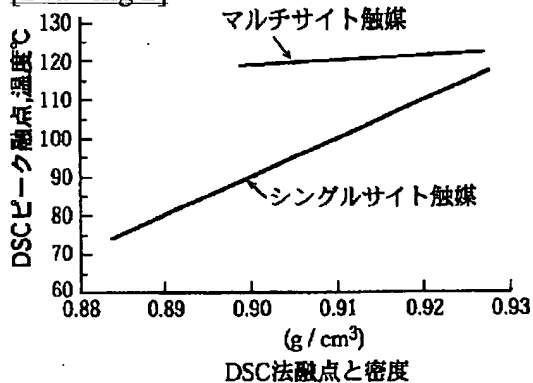
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DRAWINGS

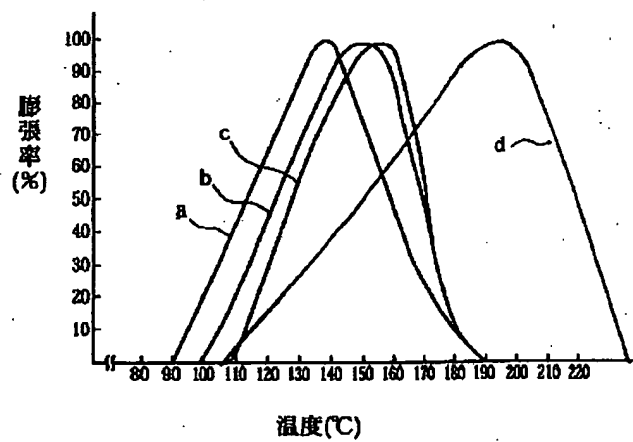
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]

PATENT ABSTRACTS OF JAPAN

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C08L 33:20

(21)Application number : 09-029691 (71)Applicant : KISHIMOTO SANGYO KK

(22)Date of filing : 28.01.1997 (72)Inventor : NAKAMURA TERUHIRO

(54) FOAMING MASTERBATCH AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a foaming masterbatch made of a base material having a low content of a low-melting sticky component and excellent mixability with an excellent affinity for a parent molding material and having excellent formability and easy handleability.

SOLUTION: A mixture is prepared by kneading heat-expandable microspheres each composed of a shell comprising a thermoplastic resin and a heat-expandable substance entrapped in the shell and a base material based on a polyethylene-type thermoplastic polymer synthesized by using a single-site catalyst by heating to a temperature in the range from the DSC peak temperature of the polyethylene-type thermoplastic polymer to the expansion initiation temperature of the microspheres. While this mixture is extruded from an extruder, it is hot-cut to form pellets.

LEGAL STATUS

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AN - 1998-489542 [42]
AP - JP19970029691 19970128
CPY - KISH-N
DC - A14 A17 E12
FS - CPI
IC - C08J3/22 ; C08J9/18 ; C08L23/04 ; C08L33/20
MC - A04-G02C A11-A04 A11-B06B A12-S04A2 A12-S09A E05-B02 E05-L E05-M E05-N
M3 - [01] A313 A923 A932 A960 G010 G019 G020 G021 G029 G040 G100 G111 G112
G113 G221 G299 M121 M122 M124 M129 M144 M148 M149 M210 M211 M212 M213
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M280 M281 M282 M283 M320 M411 M510 M520 M530 M531 M532 M533 M540 M620
M630 M782 M903 M904 Q130; 9842-HBI01-K 9842-HBI01-M
- [02] A313 A921 A960 M210 M211 M250 M283 M320 M411 M510 M521 M530 M540
M620 M630 M782 M903 M904 Q130; 9842-HBI02-K 9842-HBI02-M
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- [04] A332 A422 A423 A540 A672 A922 A940 B605 B615 B720 B751 B803 B813
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C807 G000 G030 G032 G211 G551 G640 M124 M125 M126 M131 M141 M142 M143
M144 M320 M411 M414 M415 M510 M520 M531 M540 M541 M610 M630 M640 M650
M782 M903 M904 Q130; 9842-HBI04-K 9842-HBI04-M
PA - (KISH-N) KISHIMOTO SANGYO CO
PN - JP10212372 A 19980811 DW199842 C08J9/18 009pp
PR - JP19970029691 19970128
XA - C1998-147589
XIC - C08J-003/22 ; C08J-009/18 ; C08L-023/04 ; C08L-033/20
AB - J10212372 A process for preparing foaming masterbatch (X) comprises:
(1) a kneading step where a thermoexpandable microsphere comprising a
thermoplastic shell and a thermoexpandable material included in the
shell and a base material comprising, mainly, a thermoplastic
polyethylene polymer synthesised by using a single site catalyst are
kneaded to give a mixture; and (2) a foaming masterbatch
pellets-preparing step where the mixture is extruded through an
extruder, hot cut, and pelletised to give a foaming masterbatch.
- ADVANTAGE - (X) has a good foaming mouldability.
- (Dwg.0/3)
CN - 9842-HBI01-K 9842-HBI01-M 9842-HBI02-K 9842-HBI02-M 9842-HBI03-K
9842-HBI03-M 9842-HBI04-K 9842-HBI04-M
IW - PRODUCE FOAM MASTERBATCH COMPRISE KNEAD THERMO EXPAND MICROSPHERE
MATERIAL EXTRUDE MIXTURE HOT CUT PELLET FOAM MASTERBATCH
IKW - PRODUCE FOAM MASTERBATCH COMPRISE KNEAD THERMO EXPAND MICROSPHERE
MATERIAL EXTRUDE MIXTURE HOT CUT PELLET FOAM MASTERBATCH
NC - 001
OPD - 1997-01-28
ORD - 1998-08-11
PAW - (KISH-N) KISHIMOTO SANGYO CO
TI - Production of foaming masterbatch - comprises kneading a
thermo:expandable microsphere and material, and extruding the mixture,
hot cutting and pelletising to give a foaming masterbatch

A01 - [001] 018 ; R00326 G0044 G0033 G0022 D01 D02 D12 D10 D51 D53 D58 D82 ;
 H0317 ; S9999 S1309-R ; L9999 L2573 L2506 ; H0000 ; S9999 S1547
 S1536 ; P1150 ; P1161 ;
 - [002] 018 ; R00326 G0044 G0033 G0022 D01 D02 D12 D10 D51 D53 D58 D82 ;
 R00936 G0044 G0033 G0022 D01 D02 D12 D10 D51 D53 D58 D88 ; H0022
 H0011 ; L9999 L2528 L2506 ; H0317 ; S9999 S1309-R ; S9999 S1547
 S1536 ; P1150 ;
 - [003] 018 ; R00326 G0044 G0033 G0022 D01 D02 D12 D10 D51 D53 D58 D82 ;
 R00817 G0475 G0260 G0022 D01 D12 D10 D26 D51 D53 D58 D83 F12 ; H0022
 H0011 ; H0317 ; L9999 L2528 L2506 ; S9999 S1309-R ; S9999 S1547
 S1536 ; P1150 ; P0088 ;
 - [004] 018 ; ND02 ; ND07 ; N9999 N6439 ; N9999 N6326 ; N9999
 N5970-R ; N9999 N6597 N6586 ; N9999 N6086 ; B9999 B3623 B3554 ;
 B9999 B5607 B5572 ;
 - [005] 018 ; D01 D05 D31 D74 D62 D61 D68 D70 D71 D18-R 7A-R Ti 4B Tr
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 - [006] 018 ; C999 C124 C113 ; C999 C293 ;
 - [007] 018 ; R00428 D01 D02 D10 D11 D50 D85 ; R00355 D01 D02 D11 D10
 D50 D84 ; A999 A282 A260 ;
 A02 - [001] 018 ; P1923 P1912 D01 D10 D11 D50 D68 D81 Al 3A O- 6A ; C999
 C124 C113 ;
 - [002] 018 ; ND01 ; Q9999 Q6917 ;